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PAPER

SBA-15-functionalized palladium complex partially confined with ionic liquid: an efficient and reusable catalyst system for aqueous-phase Suzuki reaction†

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A novel SBA-15 functionalized palladium complex partially confined with 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (Material **4**) was found to be a very efficient and reusable catalyst in the Suzuki–Miyaura coupling reaction of aryl halides including aryl chlorides and heteroaryl halides with different aryl boronic acids under aqueous conditions without any organic co-solvents. Our studies showed that **4** is a more efficient catalyst in comparison with the catalyst not containing IL or catalyst with a higher ratio of IL. The materials were characterized by N_2-sorption analysis, TGA and transmission electron microscopy before and after catalysis. While our studies showed that the catalyst can be successfully recycled and reused in at least 4 reaction runs, in contrast, several poisoning experiments and kinetic studies provide the notion that homogeneous (dissolved) species are responsible for the observed catalysis.

Introduction

The Suzuki–Miyaura cross-coupling of boronic acids or esters with organic halides is one of the most important transformations in organic chemistry for the construction of biaryl units from both an academic and industrial point of view.[1–8] Biaryls are valuable compounds used in production of fine and bulk chemicals such as pharmaceuticals, agrochemicals and natural products.[9–17] While the Suzuki coupling has been traditionally performed using palladium catalyst in the presence of various phosphine ligands under homogeneous conditions, they suffer from the problems of separation of catalyst from reaction mixture, recycling of catalyst, deactivation through the aggregation of metallic Pd particles, and product contamination, which is particularly drawback for pharmaceutical industries.[1,2] Hence efforts have been made to immobilize the homogeneous palladium catalysts onto a diverse solid supports in the form of either metal complex and metal nanoparticles in order to facilitate their separation from the products.[13–16] Furthermore, heterogeneous catalysts with reasonable recyclability, which is the key factor for the practical applications, are still limited. However, the major problem when using metal nanoparticles as catalysts in coupling reactions is their aggregation into less active large particles due to the high surface energy of the nanoparticles. Therefore, one of the most challenging topics in this area is the development of more appropriate heterogeneous systems to effectively to prevent the aggregation and agglomeration of Pd nanoclusters while keeping their durable activity in coupling reactions.

In recent years, it has been revealed that the use of ionic liquid functional groups either grafted[17–19] or impregnated on the solid supports played an important role in preventing the aggregation of Pd nanoparticles.[20–26] Among different supports, ordered mesoporous materials are very attractive for immobilizing palladium catalysts, because of their large pore size (1.5–40 nm), high surface area (up to 2000 m^2 g^{-1}), and tunable structure.[27–31]

Quite recently, we showed that the confinement of the ionic liquid 1-butyl-3-methylimidazolium bromide ([BMIm] Br) inside the nanospace of SBA-15-functionalized TEMPO resulted in an efficient catalyst system for aerobic oxidation of alcohols.[32] Our investigation revealed that using this combined catalyst system much higher selectivities can be attained in the oxidation of allylic alcohols in comparison with SBA-15-TEMPO not charged with IL.[32] In continuation of this study, herein, we show that the partial confinement of nanospaces of a novel SBA-15-functionalized palladium complex with 1-butyl-3-methylimidazolium hexafluorophosphate significantly improves the catalyst performance and the catalyst selectivity in the Suzuki–Miyaura coupling of aryl halides with aryl boronic acids in water.

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† Electronic supplementary information (ESI) available: The experimental details for the preparation of catalyst **4**, N_2 adsorption-desorption isotherms and TGA analysis of catalyst **4** and all intermediates, ^{1}H- and ^{13}C-NMR for all coupling products. See DOI: 10.1039/c2ob07176b

Results and discussion

The preparation procedure to obtain the catalyst is outlined in Scheme 1. We chose to employ the ordered mesoporous silica SBA-15[29,30] as a support for a bidentate ligand because it has regular porosity, high surface area, and high thermal and hydrothermal stabilities. SBA-15 was obtained in the presence of pluronic P123 ($EO_{20}PO_{70}EO_{20}$, EO = ethylene oxide, PO = propylene oxide, M_{AV} = 5800, Aldrich) as a lyotropic structure directing agent and $(EtO)_4Si$ as silica precursor under acidic conditions following the reported literature procedure.[30] The resulting SBA-15 was then functionalized with 3-aminopropyltrimethoxysilane followed by the condensation with 2-acetylpyridine using known procedures[33] to give the corresponding iminopyridine functionalized SBA-15 **2**. The obtained iminopyridine functionalized SBA-15 was then reacted with an acetone solution of $Pd(OAc)_2$ at room temperature, as described in the Experimental, affording the immobilized palladium complex (**SBA-15-Pd**, **3**). To this end, **3** was allowed to mix with an acetone solution of 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIm][PF_6]$ with appropriate concentration (1 g IL in 0.5 ml acetone). After stirring for 24 h and evaporation of the volatile solvent under reduced pressure, eventually yield a free-flowing brown solid, which is referred to as **IL@SBA-15-Pd 4** (Scheme 1).

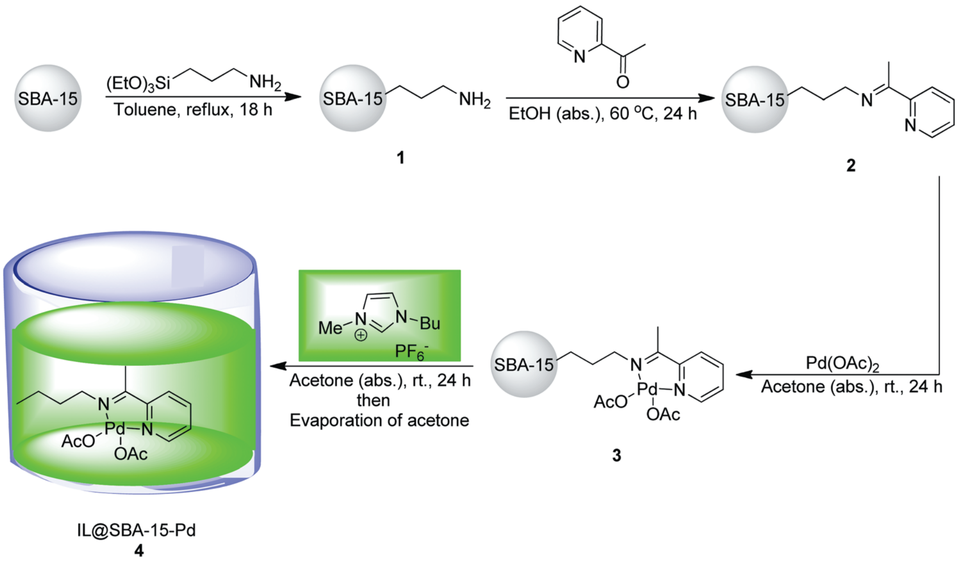
For the purpose of comparison, a diverse array of SBA-15 supported palladium catalyst was prepared by the confinement of other ionic liquids bearing alkyl chain functionality in order to study the effect of alkyl chains in the confined ionic liquid on catalyst activity.

The textural properties of the original palladium supported SBA-15 **3** were measured by nitrogen adsorption–desorption isotherm at 77 K (Fig. 5S, ESI†). The material exhibited a type IV isotherm with sharp hysteresis loop in relative pressures $P/P_0 \approx$ 0.6–0.8, which is the characteristic of ordered mesoporous material with open pore structure and a narrow pore size distribution. The calculated Brunauer–Emmett–Teller (BET) surface area, Barrett–Joyner–Halenda (BJH) average pore size distributions and primary mesoporous volume were shown to be 599 $m^2\ g^{-1}$, 8.2 nm and 0.99 $cm^3\ g^{-1}$, respectively.[34] On the other hand, **IL@SBA-15-Pd 4** display considerably lower BET surface area, and primary mesoporous volume in comparison to **SBA-15-Pd**. It is also worth nothing that the BJH average pore size of **4** was also slightly decreased by 6.7 nm. These results suggest that ionic liquid $[BMIm][PF_6]$ were successfully introduced into the interior of nanospaces of SBA-15, where covalently immobilized palladium complexes are located.

The results also point to the fact that the mesopores of the material **4** are not fully filled by the ionic liquid (Fig. 5S *vs.* 6S, ESI†). The thermal stability of both **3** and **4** was determined by thermogravimetric analysis (TGA) with heating from room temperature to 800 °C under an air flow. The organic materials present in **3** were also determined by elemental analysis. Finally the Pd content of all prepared catalysts was calculated using atomic absorption spectroscopy of the acid washed solution using standard addition method. The catalytic performance of **4** was then evaluated in the Suzuki–Miyaura coupling reaction of arylboronic acids with various types of aryl halides in water. The reaction was initially tested using 4-bromoanisole and phenylboronic acid coupling partners and K_2CO_3 as base in neat water at 60 °C (Table 1).[35] As shown in Table 1, **4** is a more efficient catalyst in comparison with the catalyst not containing IL (Table 1, entry 4) or catalyst having higher ratio of IL to **SBA-15-Pd** (**SBA-15-Pd**/IL = 1 g/1 g, Table 1, entry 5).

Also the results showed that the use of catalysts containing *n*-octyl and *n*-dodecyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium bromide gave a much lower yields of the corresponding products (Table 1, entries 2, 3 and 6).

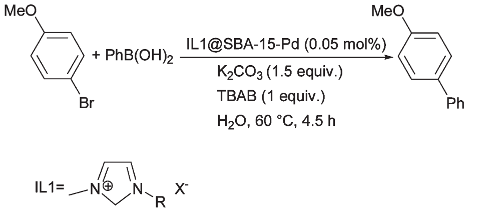
The resulting **IL@SBA-15-Pd** (IL = 1-butyl-3-methylimidazolium hexafluorophosphate) catalyst was then tested in the Suzuki cross-coupling reaction of arylboronic acids with various types of aryl halide under similar reaction conditions. The reactions were conveniently carried out in a batch reactor in the



Scheme 1 A schematic pathway for preparation of SBA-15-functionalized palladium complex partially confined with $[BMIm][PF_6]$ as ionic liquid.

temperature range 60–90 °C. As expected, we observed that the coupling of 4-iodoanisole (1 mmol) and phenylboronic acid (1.1 mmol) in the presence of **IL@SBA-15-Pd** (0.05 mol%) and K_2CO_3 (1.5 mmol) in distilled water (3 mL) at 60 °C proceeded rapidly to give 4-phenylanisole in 92% isolated yield after 2 h (Table 2, entry 1). We then investigated Suzuki coupling reaction of aryl bromides using **4** as the catalyst. As shown in Table 2, the reactions of various aryl bromides including electron-rich (deactivated) and electron-deficient (activated) substrates proceeded readily at very low catalyst loading (0.05–0.1 mol%) in water to afford excellent yields of the corresponding biphenyls (Table 2, entries 3–10).

Table 1 Suzuki–Miyaura coupling of 4-bromoanisole with phenylboronic acid using various type of IL confined **SBA-15-Pd** catalyst systems



Entry	R	X	Loading of IL (g IL/g **3**)	Yield (%)
1[a]	**^{n}Bu**	**PF_6**	**0.5**	**95**
2	^{n}Oct	PF_6	0.5	41
3	^{n}Dodec	PF_6	0.5	23
4[b]	—	—	—	58
5	^{n}Bu	PF_6	1	33
6	^{n}Bu	Br	0.5	69

[a] IL@SBA-15-Pd **4**. [b] SBA-15-Pd **3**.

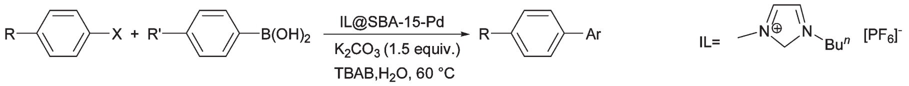
We found also that catalyst **4** (0.2 mol%) shows high reactivity for Suzuki–Miyaura cross-coupling of activated aryl chlorides with phenyl and *p*-tolyl boronic acid in water (Table 2, entries 11 and 12). Since many drugs contain heteroaromatic fragments chemists are very interested in cross-coupling of heteroaryl halides, but the presence of heteroatoms such as sulfur and nitrogen often leads to low reactivity in transition-metal catalyzed coupling reactions.[36] Along this line, commercially available, substrates, 3-bromo pyridine, 2-bromo pyridine and 2-bromo thiophene were tested (Table 2, entries 13–17). These substrates were found to give an excellent yield of the Suzuki product without loss of activity of catalyst. Moreover, various functional groups, such as cyano, acyl, CHO, ethyl, and methoxy were tolerated and the corresponding coupled products were obtained in excellent isolated yields (Table 2, entries 1–12).

It should be also noted that performing the Suzuki–Miyaura cross-coupling of 4-bromoanisol with phenyl boronic acid in open air resulted in almost the same yield of cross-coupling product (Table 2, entry 10) in comparison with the same transformation performed under an argon atmosphere (*ca.* 97%), confirming that the atmosphere does not significantly impact on the efficiency of the present catalyst system.

The reusability and recovery of the catalysts are important issues, especially when the reactions use solid catalysts. By using the coupling reaction of phenylboronic acid and 4-bromo benzaldehyde as a test model, it was found that this supported catalyst has been recovered and reused up to 4 times without considerable loss of its reactivity (1st reuse: 95%, 2nd reuse: 93%, 3rd reuse: 96%, 4th reuse: 90%, Fig. 1).

To assess whether the catalyst is actually operating in a heterogeneous pathway, or whether it is merely a reservoir for more active or naked Pd nanoparticles, a set of three independent experiments including a Hg^0 test and two three-phase poisoning tests were designed for the coupling reaction of 4-bromoanisole

Table 2 Suzuki–Miyaura coupling of aryl halides with aryl boronic acids using **IL@SBA-15-Pd**, **4**



Entry	X	R	R′	**IL@SBA-15-Pd** (mol%)	TBAB[a] (equiv.)	Time (h)	Yield[b] (%)
1	I	MeO	H	0.05	—	2	92
2	I	Me	Me	0.05	—	2	96
3	Br	CHO	H	0.05	—	2	95
4	Br	CN	H	0.05	—	2	93
5	Br	CN	Me	0.05	—	2	95
6	Br	NO_2	H	0.05	—	2	100
7	Br	NO_2	Me	0.05	—	2	96
8	Br	H	H	0.05	0.5	4	100
9	Br	Me	Me	0.05	0.5	4	92
10	Br	MeO	H	0.05	1	4.5	95
11	Cl	NO_2	H	0.2	2	10	84[c]
12	Cl	NO_2	Me	0.2	2	10	90[c]
13	3-Bromopyridine		H	0.1	1	8	94[c]
14	3-Bromopyridine		Me	0.1	1	8	99[c]
15	2-Bromothiophene		H	0.1	1	10	99[c]
16	2-Bromothiophene		Me	0.1	1	10	97[c]
17	2-Bromopyridine		H	0.1	1	8	91[c]

[a] TBAB: tetra butyl ammonium bromide. [b] Isolated yields. [c] Temperature: 80 °C.

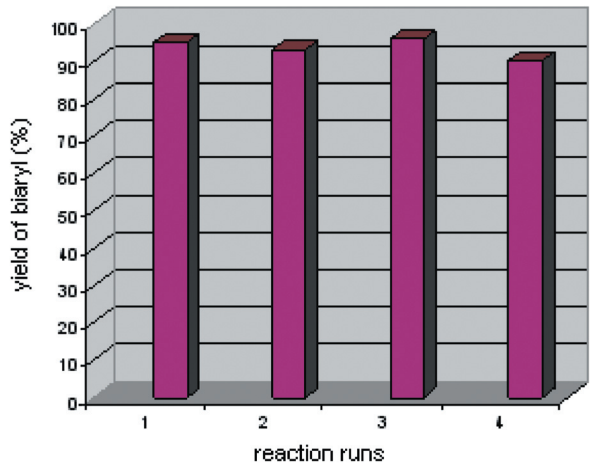


Fig. 1 Representation of 4-phenyl benzaldehyde yield at different reuses of the catalyst.

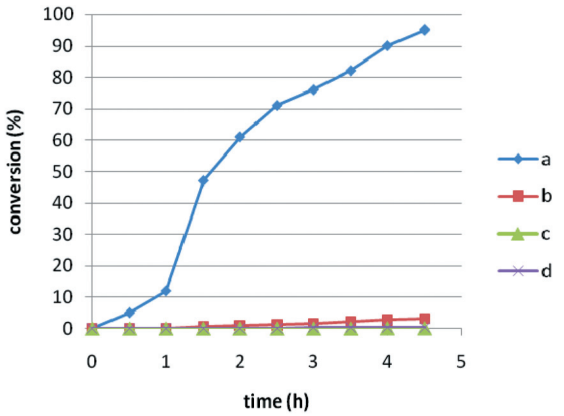


Fig. 2 Reaction progress as a function of time for the Suzuki coupling of 4-bromoanisole with phenylboronic acid by using **IL@SBA-15-Pd** catalyst in water under: (a) normal conditions (blue diamond), (b) in the presence of 400 equiv. Hg^0 (red square), (c) in the presence of 400 equiv. PVP (violet cross), and (d) in the presence of 400 equiv. mercaptopropyl silica (green triangle).

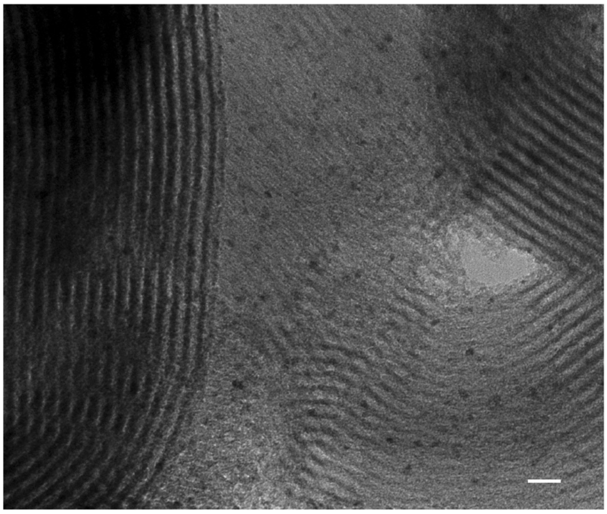


Fig. 3 Transmission electron microscopy (TEM) image of recovered **IL@SBA-15-Pd** material showing two dimensional hexagonal symmetry with superior uniformity of the mesoporous channels. Scale bar: 20 nm.

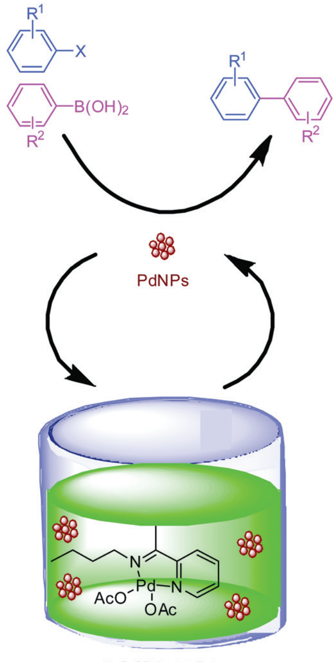
with phenyl boronic acid under the standard reaction conditions.[37,38] To conduct the test, three different flasks were charged with 4-bromoanisole (1 mmol), phenyl boronic acid (1.1 mmol), **IL@SBA-15-Pd** (0.05 mol%), and K_2CO_3 (1.5 mmol) in water (3 mL) as the solvent. The mixture of three flasks were then heated to 60 °C, while mercury (Hg^0) was added to the first flask, amorphous silica-supported mercaptopropyl (mercaptopropyl silica) to the second one, and poly-(4-vinylpyridine) (PVP) to the third flask in a ratio of 400 equiv. to the initial palladium content of the catalyst. These control experiments showed that the reactions were quenched completely over all three flasks upon addition of the poison (Fig. 2). These results suggest that for the present reaction, supported palladium catalyst serves as a reservoir for active Pd species that are dissolved from the solid catalyst under the described reaction conditions.

To further study the contribution of homogeneous catalysis, we also conducted a hot-filtration test after the reaction of 4-bromoanisole with phenyl boronic acid was initiated and before the substrates were consumed. We found that a further 21% conversion of the coupling reaction was observed upon the heating of the catalyst-free solution for 24 h at 60 °C. The positive hot-filteration test is certainly in good agreement with the results obtained from the poisoning tests and highlight the notion that **IL@SBA-15-Pd** catalyst system is indeed a pre-catalyst for the soluble (homogeneous) palladium species in the described Suzuki–Miyaura coupling reaction.

To understand the changes in our catalyst system on a molecular level during the reaction, the recovered catalyst was further subjected to N_2-adsorption–desorption analysis, transmission electron microscopy (TEM) and elemental microanalysis. N_2-sorption studies and TEM analysis provide valuable information about the surface properties and ultrastructure of the recovered catalyst. It is noteworthy that even after the reaction and recycling, the recovered catalysts exhibit a type IV isotherm with a sharp condensation–evaporation stage, which indicates that the ordered mesostructures have mostly survived. Notably, the materials also showed a total pore volume slightly lower than that of the fresh catalyst charged with ionic liquid. While this result indicates a partial desorption of ionic liquid during the catalysis and work-up stages, it strongly points to the fact that the total loss of ionic liquid [BMIm][PF_6] was still not significant in the recovered catalyst.[34]

Both TGA and elemental microanalysis demonstrate that the loss of ionic liquid is not significant (less than 5% after the 4th reaction cycle), which could account to some extent the preservation of catalytic activity during 4 reaction runs.

TEM image of the catalyst after the 4th reaction cycle is displayed in Fig. 3. This micrograph demonstrates that not only the 2D-hexagonal structure of the catalyst is largely survived but also a well-distribution of Pd nanoparticles with sizes mostly less than 5 nm throughout the regular channels of the parent SBA-15. This observation reveals, interestingly, that while



4

Scheme 2 The proposed pathway for the generation, stabilization, and re-capture of Pd-nanoparticles into the interior of the mesochannels of **4** where the physically adsorbed ionic liquid [BMIm][PF_6] layer is located.

IL@SBA-15-Pd acts as a reservoir for highly active and soluble Pd species, it may also operate as a nanoscaffold to recapture Pd nanoparticles inside the mesopores where ionic liquid are located as stabilizer, thus preventing Pd aggregation (Fig. 3).

The result of TEM analysis accompanied with our complimentary kinetic and poisoning experiments revealed that while catalyst system **4** could in fact act as a reservoir for the soluble palladium species in the described Suzuki–Miyaura coupling protocol but it is also a powerful support for the stabilization of re-captured active Pd-nanoparticles (PdNPs) in the interior of SBA-15 mesochannels where physically adsorbed ionic liquid layer is located (Scheme 2).

Conclusions

We have demonstrated that a novel SBA-15 functionalized palladium complex partially confined with imidazolium type ionic liquids efficiently catalyzes Suzuki–Miyaura coupling of aryl halides. This reusable catalyst is also quite effective for the coupling of heteroaryl halides. Interestingly, it was found that while hot filtration tests and kinetic experiments showed the presence of soluble Pd species during the reaction process, recovery studies illustrated that no significant decrease has occurred in the activity and metal content of recovered **IL@SBA-15-Pd**. This observation implies that while catalyst system **4** could in fact act as a reservoir for the soluble palladium species in the described Suzuki–Miyaura coupling protocol, it is also a powerful support for the generation and stabilization of active Pd-nanoparticles (PdNPs) in the interior of SBA-15 mesochannels where physically adsorbed ionic layers are located.

Experimental

Preparation of SBA-15

The synthesis of SBA-15 has been achieved using a known procedure described by Stucky and co-workers (see ref. 30). In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average M_w = 5800) was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 35 °C. Then 8.50 g of tetraethoxysilane (TEOS) was added into that solution while stirring at 35 °C for 20 h. The mixture was aged at 80 °C overnight without stirring. The solid was filtered off and washed thoroughly with hot ethanol/water using a Soxhelet apparatus for 18 h to remove the surfactant molecules. It was dried in air at 110 °C overnight.

Preparation of SBA-15-amine

Refluxing the SBA-15 (10 g) with 3-aminopropyltrimethoxysilane (10 mmol) in dry toluene for 18 h. The solid materials were filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhelet) and then dried in oven at 90 °C overnight to give the SBA-15 supported amine (SBA-15-amine).

Preparation of SBA-15-lig

2-Acetylpyridine (0.97 g, 8 mmol) was added to a mixture of the oven dried SBA-15-amine (5 g) in super dry ethanol (150 mL) in a 250 mL round bottomed flask. The reaction mixture was stirred at 60 °C for 24 h. The ligand-grafted silica was filtered at the reaction temperature and the resulting solid was washed thoroughly with hot toluene and ethanol to remove unreacted ketone. It was dried in air at 90 °C overnight to furnish the corresponding SBA-15 supported bidentate ligand (SBA-15-lig).

Preparation of SBA-15-Pd

SBA-15-lig (3 g) was added to a solution of palladium acetate (0.035 g Merck) in dry acetone (100 mL). The reaction mixture was stirred at room temperature for 24 h. After stirring, the solid was filtered, washed with acetone, ethanol and ether in order to remove any adsorbed palladium on the surface. It was then dried in an oven at 90 °C overnight to furnish the corresponding SBA-15 supported complex (**SBA-15-Pd**).

Preparation of IL@SBA-15-Pd

SBA-15-Pd (3 g) was added to a solution of 1-butyl-3-methylimidazolium hexafluorophosphate (1.5 g) in dry acetone (100 mL). The reaction mixture was stirred at room temperature for 24 h. After stirring, acetone was slowly removed under reduced pressure. The resulting powder was then dried in an oven at 90 °C overnight to give final catalyst **IL@SBA-15-Pd** at a loading *ca.* 0.032 ± 0.001 mmol g^{-1} (atomic absorption spectroscopy (AA)).

General procedure for heterogeneous Suzuki reaction

The Suzuki reaction was performed by using arylboronic acid (1.1 mmol), aryl halide (1.0 mmol), K_2CO_3 (1.5 mmol), and catalyst (0.05–0.2 mol%) in distilled water at 60–80 °C. The reaction progress was monitored by GC analysis after completion of the reaction; the mixture was allowed to cool to room temperature and was then filtered and washed with H_2O and ethyl acetate. The organic phase was separated and dried over $MgSO_4$ and the solvent was then removed under reduced pressure. Pure products were obtained after recrystallization or by isolation of the residue by column chromatography on silica.

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34 See ESI† for details.

35 The amounts of ionic liquid needed to partially fill the nanospace of **SBA-15-Pd 3** were optimized based upon the activity of **IL@SBA-15-Pd 4** comprising different volume of [BMIm][PF_6] in a typical Suzuki coupling reaction of 4-bromoanisole with phenylboronic acid under the described reaction protocol in the Experimental.

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